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CHEMICAL ABSTRACTS 116(12):1163896
CHEMICAL ABSTRACTS 95(24):213739W

(58) Field of search
UK CL (Edition L) **C1A APF9B AVG1**
INT CL[5] **C01G, C23C**
On line databases: W.P.I. CLAIMS

(54) **Doped potassium tantalum niobate**

(57) A composition, for use in preparing a film, (preferably an epitactic film) comprising a solid solution of $KNbO_3$ and $KTaO_3$ forming a product of formula I

$$K_{1-Y}M_YTa_{1-X}Nb_XO_3 \qquad (I)$$

in which M is a monovalent metal ion other than K^+ (hereinafter defined as the dopant) eg Na^+, Li^+ or Ag^+;

y = 0.02 to 0.20 and

x = 0.05 to 0.95.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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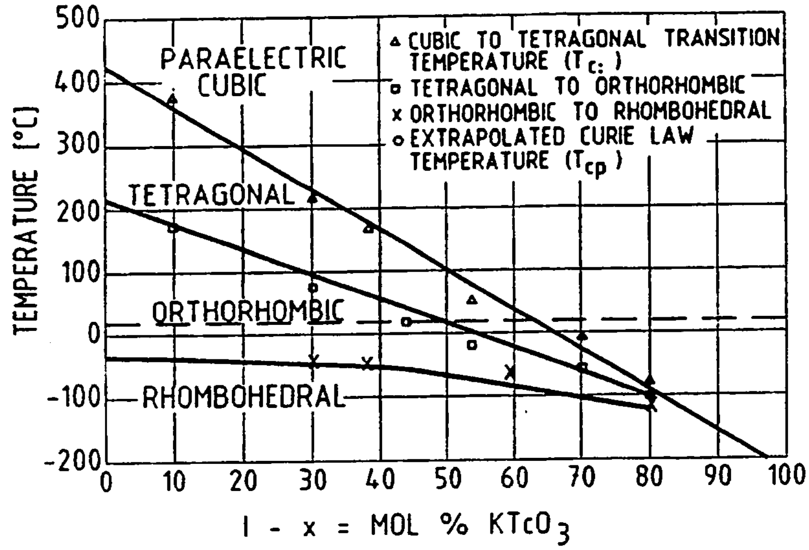
FIG. 1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100
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-100
-200
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TETRAGONAL
ORTHORHOMBIC
RHOMBOHEDRAL
▵ CUBIC TO TETRAGONAL TRANSITION TEMPERATURE (T_c)
▫ TETRAGONAL TO ORTHORHOMBIC
x ORTHORHOMBIC TO RHOMBOHEDRAL
o EXTRAPOLATED CURIE LAW TEMPERATURE (T_{cp})
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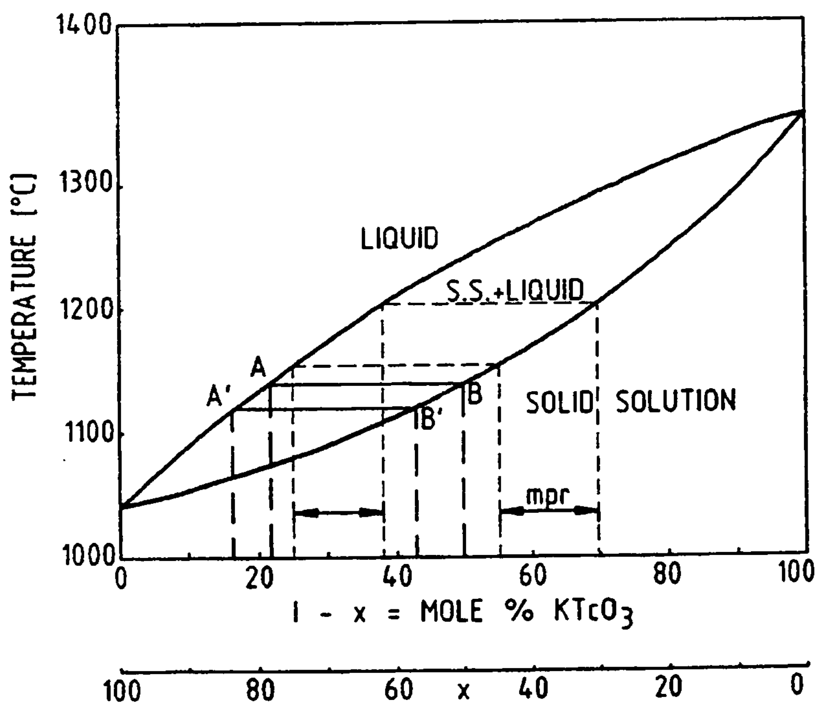
1 - x = MOL % $KTcO_3$

FIG. 2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1200
1100
1000
TEMPERATURE [°C]
LIQUID
S.S.+LIQUID
A
A'
B
B'
SOLID SOLUTION
mpr
0 20 40 60 80 100
1 - x = MOLE % $KTcO_3$
100 80 60 x 40 20 0

FILMS OF KTN AND $KTaO_3$

The invention relates to compositions capable of producing film on a substrate, to methods for producing such films and to films produced thereby. Such films are preferably epitaxial films of KTN ($KTa_{1-x}Nb_xO_3$).

According to the invention there is provided a composition, for use in preparing a film (preferably an epitactic film) comprising a solid solution of $KNbO_3$ and $KTaO_3$ that forms a product of formula I

$$K_{1-y}M_yTa_{1-x}Nb_xO_3 \qquad \text{(I)}$$

in which M is a monovalent metal ion other than K^+ (hereinafter defined as the dopant);

y = 0.02 to 0.20 and

x = 0.05 to 0.95.

The product of formula I is known as KTN, doped with metal M.

Generally the dopant is a monovalent ion.

Preferably the dopant is selected from alkali metals (other than K^+) and Ag^+. More preferably the dopant is selected from Na^+, Li^+ and Ag^+.

Preferably in a composition according to the invention, x is 0.2 to 0.85, more preferably 0.2-0.7, most preferably 0.2-0.6, especially 0.3 to 0.45.

Preferably to produce a ferroelectric film, x is 0.4 to 0.6 in the composition of the solid solution.

Preferably to produce a paraelectric film, x is 0.3 to 0.4.

The terms "ferroelectric" and "paraelectric" are terms of the art and are defined in Phys. Rev. 114 (1959) 63 et. seq., the contents of which are incorporated herein by reference.

Figure 1 shows the various phases of KTN in a diagram temperature vs. composition.

Preferably for cubic paraelectric layers, x is 0.6-0.7, preferably 0.68 in the liquid.

Preferably, for tetragonal ferroelectric layers, x is 0.7 to 0.85, more preferably 0.75 to 0.85, most preferably 0.82.

Figure 2 shows the liquid, mixed (solid solution + liquid) and solid (the solid solution refers to a completely miscible solid of $KTaO_3$-$KNbO_3$ mixed material, i.e. KTN) phases as a function of temperature and composition.

Further according to the invention, there is provided a substrate on which a product of formula I

$$K_{1-y}M_yTa_{1-x}Nb_xO_3 \qquad \text{(I)}$$

in which M is a monovalent metal ion other than K^+;

$y = 0.02$ to 0.20 and

$x = 0.05$ to 0.95;

has been applied as a film or coating layer.

Such substrates include metals (e.g. Pt or Au) and crystals such as $KTaO_3$ ($KTaO_3$ is the most preferred substrate). Preferred substrates are those having a lattice constant of 3.8-4.2, more preferably 3.9-4.10, most preferably 3.9883.

The film may be applied either over the whole surface of the substrate or over a part of the surface.

Preferably the composition produces one homogeneous built-up layer with periodic arrangement of the atoms with the same periodicity as the crystal lattice on the surface of the substrate (e.g. a crystal).

It has been found that this composition yields films having substantially reduced (or being substantially free from) misfit dislocations with the substrate, especially when the substrate is $KTaO_3$.

Misfit dislocations are well known in the art and occur when the lattice constant difference of the substrate differs sufficiently from that of the film.

Still further according to the invention there is provided a solution, for producing an epitactic film on a substrate having lattice constant of 3.8-4.2, comprising a product of formula I

$$K_{1-y}M_yTa_{1-x}Nb_xO_3 \qquad \text{(II)}$$

in which
M is a monovalent ion other than K^+;
x is 0.05-0.95; and
y is 0.02 to 0.20;

in a solvent system selected from KF/NaF, KF/LiF, K_2O/Na_2O, K_2O/Li_2O, K_2MoO_4/Na_2MoO_4 and K_2MoO_4/Li_2MoO_4. (Preferably a true solution is formed).

Preferably about 0.05% of the total amount of KTN in the solution or about 5 mg of KTN

is required per cm^2 per layer thickness where the layer is 0.1-100μm, more preferably 1-20μm, most preferably about 10 μm.

Preferably from such a solution, the resulting film has 2 to 20 mol% of K^+ ion replaced by dopant ions, i.e. Na^+ or Li^+.

The preferred solvent, when a thin film is required, is selected from KF/NaF and KF/LiF. The preferred solvent when a thick film is required is selected from K_2O/Na_2O and K_2O/Li_2O.

Preferably in a solution according to the invention, a KF/NaF or KF/LiF solvent system comprises 80-98mol% and KTN 20-2 mol%. Alternatively KTN comprises 90-99 mol% and a K_2O/Na_2O or K_2O/Li_2O solvent system 10-1 mol%. The amount of dopant containing solvent (e.g. NaF or LiF or Na_2O or Li_2O respectively) in the solvent system is 2-20 mol%, based on the weight of the solvent system.

A most preferred solution is KTN 5-10 mol% and 90-95 mol% of a solvent system (or solution) of KF and NaF (KF being from 80-98 mol% and NaF being from 2-20 mol% of said solvent system).

Yet further according to the invention there is provided a process for preparing one or more film layers (preferably epitactic) on the surface of a substrate, the substrate having having a lattice constant of 3.8-4.2, comprising

i) dissolving 5-95mol% of $KNbO_3$ and 95-5mol% of $KTaO_3$ in a solvent selected from KF/NaF, KF/LiF, K_2O/Na_2O, K_2O/Li_2O, K_2MoO_4/Na_2MoO_4, and K_2MoO_4/Li_2MoO_4; and

ii) immersing or dipping the substrate in said solution at an elevated temperature.

The preferred elevated temperature is from 860 to 1200 °C.

Preferably the thickness of the layer is from 0.5 to 200µm, more preferably 1-5µm (thin films) or 50-200µm (thick films).

Further according to the invention, there is provided a $KTaO_3$ crystal to which a film has been applied, preferably an epitactic film, the film composition comprising

i) 5-95 mol% $KNbO_3$
ii) 95-5 mol% $KTaO_3$

and containing 2 to 20 mol% of K^+ ion replaced by dopant (as herein before defined).

The substrates, especially $KTaO_3$ crystals, to which a film according to the invention has been applied can be used in the field of integrated optics, for example in electrooptic and acoustooptic modulators for optical frequency conversion, for pyroelectric sensors (heat sensors), piezoelectric sensors or for ferroelectric memory devices.

Reference is made to the article "Nonlinear Integrated Optics" by G.I. Stegeman and C.T. Seaton in J. Appl. Phys. 58(1985) R57 with regard to integrated optics. Reference is made to the article by S.L. Swartz and V.E. Wood, in Condensed Matter News 1 (1992)5 with regard to ferroelectric memories, the contents of each of the above references being incorporated by reference.

The advantage of using the preferred solvents is that a sufficient degree of solubility of $KNbO_3$ and $KTaO_3$ is achieved whilst having a reasonable melting point and at the same time allowing for supercooling between 30 and 100°C.

For non-lattice-matched layers, eg where f (the lattice constant difference)>10^{-3}

$$f = \frac{a_L - a_S}{a_S}$$

where

a_L is the lattice constant of the layer and

a_S lattice constant of the substrate,

a pronounced defect pattern can be seen, induced by lattice relaxation by cooling down to room temperature after growth. These defects can be overcome by the present invention. Should color occur in the layers (due to the highly reductive nature of KF for example) this can be removed by annealing in O_2.

According to the invention there is also provided a pyroelectric sensor or ferroelectric memory device containing a $KTaO_3$ crystal coated with an epitactic film comprising

a) 5-95 mol% of $KNbO_3$ and
b) 95-5 mol% $KTaO_3$

containing 2 to 20 mol % of a monovalent metal other than K^+ (hereinafter defined as the dopant).

For use in a ferroelectric device, KTN is grown on $KTaO_3$. On top of the KTN layer, an electrode of Au or Ag may be deposited by known art methods. For a thickness of >10μ, the KTN has to be poled since the domain structure for these layer thicknesses diminishes the effective electrooptic and pyroelectric effects. For a pyroelectric device, a temperature change will induce an electric charge in the layer induced by a displacement in the internal atomic structure. This electric charge is removed by a contacted wire, which induces a signal which can be amplified and hence used as an alarm system.

In this specification, unless stated otherwise all % are mol%.

The invention will now be illustrated by the following Example.

Example

Lattice matched epitaxial $KTa_{0.71}Nb_{0.29}O_3$ (i.e., 71 mol% $KTaO_3$ + 29 mol% $KNbO_3$) layers with a Na content of 10.4 mol% (i.e 10.4% of K ions are replaced by Na ions) are grown from a solution containing 93% KF (88.5 mol%) - NaF (11.5 mol%) solvent with 7 mol% of KTN where the KTN is $KTa_{0.32}Nb_{0.68}O_3$ on a $KTaO_3$ substrate at 950-960°C. The solution containing compounds is mixed and filled into a Pt crucible. For the dissolution of KTN in the given solvent, the furnace is heated up to 1050°C with ~ 120°C/h, kept at this temperature for ~ 8-12 hours and slowly (60°C/h) cooled to the epitaxial temperature given by the flux composition and Nb concentrations. Then, after a dwelling time at the epitaxial temperature of about 30 minutes, the Pt mounted substrate is dipped into the supercooled solution for the necessary growth time, given by required film thickness. After the growth time the substrate with the film is removed from the solution and slowly (50°C/h) cooled to room temperature. After cooling, the substrate and the film are removed from the substrate holder and cleaned in water an phosphoric acid. This $KTaO_3$ crystal is described in Landolt-Boemstein, Numerical Data and Functional Relationships on Science and Technology, Group III vol. 16, Ferroelectric Oxide, the content of which is incorporated herein by reference.

A $KTaO_3$ crystal oriented along (100) of dimensions between 3x3x0.3 and 10x10x2mm is dipped into the above solution at 950-960°C. The growth time is between 5 and 30 minutes for layers of thickness between 2 and 3 microns.

The surface of the substrate on which the KTN is grown is 0.2 to 1 cm^2, thickness 10μm (about 6 mg). The amount of solvent used is as much as possible for a stable condition of the KTN solution to be formed.

The substrate is oriented parallel to a (100) plane. The growth times for 2 to 30μm thick

layer vary between 5 and 30 min. The lattice constant difference f (misfit) for lattice matched layers is $f<2.8 \pm 0.4 \times 10^{-4}$. (For non lattice matched layers with an equivalent composition, f is 1.5×10^{-3}. Such layers show a pronounced defect pattern induced by lattice relaxation by the cooling down to room temperature after growth.) Where the addition of NaF to the solvent reduces the solubility, this can be corrected by the use of higher growth temperatures of 1.2°C/mol% NaF. The coloration can be removed by annealing in O_2 at 980°C for 20 hours. The discoloration is also related to the lower fluorine content following the O_2 annealing step.

For optical measurements, such as standard waveguiding experiments, the layer surface and the head face (face perpendicular to a layer surface) are polished. Polishing of the layer surface and side face may be with a diamond paste of 1 and $^1/_4$ μm grain size.

Waveguiding experiments on non lattice matched layers show strong scattering, caused by the defect pattern. This scattering can be avoided by the lattice matching of the film of the Example. The refractive index of Na^+ doped samples are not influenced by the incorporation of Na^+.

The layer produced with this method can be used for active elements for integrated optics, e.g. as a light modulator or for optical frequency conversion devices (blue or green upconverted lasers). The process for the growth of single crystalline epitaxial layers for different optoelectronic applications can be modified when para- or ferro- electric layers of $KTa_{1-x}Nb_xO_3$ need to be grown.

For paraelectric layers the KTN content of the e.g. KF/NaF/KTN solution contains 3-8mol% KTN with a Nb content of x = 0.68

For ferroelectric layers with a Curie temperature of ~65°C, the KTN content of the e.g. KF/NaF/KTN solution contains 3-8mol% KTN with a Nb content of x = 0.82.

CLAIMS:

1. A composition, for use in preparing a film, comprising

   a solution comprising a product of formula I

   $$K_{1-y}M_yTa_{1-x}Nb_xO_3 \qquad (I)$$

   in which M is a monovalent metal ion other than K^+ (herein defined as the dopant)
   y = 0.02 to 0.20 and
   x = 0.05 to 0.95.

2. A composition according to Claim 1 in which the dopant is selected from alkali metals (other than K^+) and Ag^+.

3. A composition according to Claim 2 in which the dopant is selected from Na^+, Li^+ and Ag^+.

4. A coated substrate on which a product of formula I

   $$K_{1-y}M_yTa_{1-x}Nb_xO_3 \qquad (I)$$

   in which M is a monovalent metal ion other than K^+;
   y = 0.02 to 0.20 and
   x = 0.05 to 0.95.

   has been applied as a film or coating layer.

5. A coated substrate according to Claim 4 in which the substrate is one having a lattice

constant of 3.8-4.2.

6. A coated substrate according to Claim 5 in which the substrate comprises a metal (e.g. Pt or Au) or the substrate comprises a crystal.

7. A coated substrate according to Claim 6 in which $KTaO_3$ is the substrate.

8. A solution, for producing an epitactic film on a substrate having lattice constant of 3.8-4.2, comprising a product of formula I

$$K_{1-y}M_yTa_{1-x}Nb_xO_3 \qquad (I)$$

in which
M is a monovalent metal ion other than K^+;
x is 0.05 to 0.95; and
y is 0.02 to 0.20;

in a solvent system selected from KF/NaF, KF/LiF, K_2O/Na_2O, K_2O/Li_2O, K_2MoO_4/Na_2MoO_4 and K_2MoO_4/Li_2MoO_4.

9. A process for preparing one or more epitactic film layers on the surface of a substrate having a lattice constant of 3.8-4.2, comprising

i) dissolving 5-95% of $KNbO_3$ and 95-5% of $KTaO_3$ in a solvent selected from KF/NaF, KF/LiF, K_2O/Na_2O, K_2O/Li_2O, K_2MoO_4/Na_2MoO_4, and K_2MoO_4/Li_2MoO_4; and

ii) immersing or dipping the substrate in said solution at elevated temperature.

10. A $KTaO_3$ crystal to which a film has been applied, the film composition comprising

i) 5-95 mol% $KNbO_3$

ii) 95-5 mol% $KTaO_3$

and containing 2 to 20 mol% of a monovalent metal other than K^+ (the herein defined as the dopant).

11. A pyroelectric sensor or ferroelectric memory device containing a $KTaO_3$ crystal coated with an epitactic film comprising

a) 5-95 mol% of $KNbO_3$ and

b) 95-5 mol% $KTaO_3$

containing 2 to 20 mol %, based on the total weight of the composition, of a monovalent metal other than K^+ (herein defined as the dopant).

Pa`nts Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number
GB 9226344.1

Relevant Technical fields

(i) UK Cl (Edition L) C1A (AVG1, APF9B)

(ii) Int Cl (Edition 5) C01G; C23C

Search Examiner
C A CLARKE

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI, CHABS

Date of Search
21 JAN 1993

Documents considered relevant following a search in respect of claims 1 TO 11

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	CHEMICAL ABSTRACTS 116(12): 116389b	1 at least
X	CHEMICAL ABSTRACTS 95(24): 213739w	1 to 3 at least

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Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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&: Member of the same patent family, corresponding document.

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